



# EDGEWOOD

## CHEMICAL BIOLOGICAL CENTER

U.S. ARMY RESEARCH, DEVELOPMENT AND ENGINEERING COMMAND

ECBC-TR-628

### EVALUATION OF TITANIA NANOTUBES FOR THE REMOVAL OF TOXIC INDUSTRIAL CHEMICALS

Gregory W. Peterson  
George W. Wagner  
John J. Mahle  
Alex Balboa  
Tara L. Sewell  
Christopher J. Karwacki

RESEARCH AND TECHNOLOGY DIRECTORATE

May 2008

Approved for public release;  
distribution is unlimited.



# 20080627 024

#### Disclaimer

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorizing documents.

REPORT DOCUMENTATION PAGE				Form Approved OMB No. 0704-0188													
<small>Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.</small>																	
1. REPORT DATE (DD-MM-YYYY) XX-05-2008		2. REPORT TYPE Final		3. DATES COVERED (From - To) Feb 2008 - Mar 2008													
4. TITLE AND SUBTITLE Evaluation of Titania Nanotubes for the Removal of Toxic Industrial Chemicals				5a. CONTRACT NUMBER													
				5b. GRANT NUMBER													
				5c. PROGRAM ELEMENT NUMBER													
6. AUTHOR(S) Peterson, Gregory W.; Wagner, George W.; Mahle, John J.; Balboa, Alex; Sewell, Tara L.; and Karwacki, Christopher J.				5d. PROJECT NUMBER BA07PRO104													
				5e. TASK NUMBER													
				5f. WORK UNIT NUMBER													
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) DIR, ECBC, ATTN: AMSRD-ECB-RT-PF, APG, MD 21010-5424				8. PERFORMING ORGANIZATION REPORT NUMBER ECBC-TR-628													
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Defense Threat Reduction Agency, 8725 John J. Kingman Road, Stop 6201, Fort Belvoir, VA 22060-6201				10. SPONSOR/MONITOR'S ACRONYM(S) DTRA JSTO-CBD													
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)													
12. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.																	
13. SUPPLEMENTARY NOTES																	
14. ABSTRACT Current technology-based efforts are focusing on a nanotechnology approach to sorbent development for air purification applications. Titania nanotubes have recently been identified as extremely active under certain circumstances for decontamination of chemical warfare agents (CWAs). Furthermore, the possibility to add functional moieties to the nanotubes makes these materials an interesting candidate for evaluation against toxic industrial chemicals. This report summarizes the evaluation of titania nanotubes using nitrogen isotherm data, water and chloroethane adsorption equilibria, and ammonia, cyanogen chloride (CK), and sulfur dioxide breakthrough data.																	
15. SUBJECT TERMS <table border="0" style="width: 100%;"> <tr> <td>Nanotubes</td> <td>Titania</td> <td>Air purification</td> <td>Sorbent development</td> </tr> <tr> <td>Nanoscroll</td> <td>Isotherm</td> <td>Adsorption equilibria</td> <td>Breakthrough testing</td> </tr> <tr> <td>Nanotechnology</td> <td></td> <td></td> <td></td> </tr> </table>						Nanotubes	Titania	Air purification	Sorbent development	Nanoscroll	Isotherm	Adsorption equilibria	Breakthrough testing	Nanotechnology			
Nanotubes	Titania	Air purification	Sorbent development														
Nanoscroll	Isotherm	Adsorption equilibria	Breakthrough testing														
Nanotechnology																	
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON												
a. REPORT	b. ABSTRACT	c. THIS PAGE			Sandra J. Johnson												
U	U	U	UL	25	19b. TELEPHONE NUMBER (include area code) (410) 436-2914												

Blank



## PREFACE

The work described in this report was authorized under DTRA Project No. BA07PRO104. This work was started in February 2008 and completed in March 2008.

The use of either trade or manufacturers' names in this report does not constitute an official endorsement of any commercial products. This report may not be cited for the purposes of advertisement.

This report has been approved for public release. Registered users should request additional copies from the Defense Technical Information Center; unregistered users should direct such requests to the National Technical Information Service.

## Acknowledgments

The authors thank Professor Dr. Yue Wu (University of North Carolina) for providing the titania nanotubes. Dr. David Tevault (U.S. Army Edgewood Chemical Biological Center) and Paulette Jones (Science Applications International Corporation) are thanked for analyzing the data and reviewing the report.

Blank

## CONTENTS

1.	INTRODUCTION .....	1
2.	EXPERIMENTAL PROCEDURES .....	1
2.1	Samples Evaluated .....	1
2.2	Testing Protocol .....	3
3.	RESULTS AND DISCUSSION .....	6
3.1	Packing Density .....	6
3.2	Nitrogen Isotherm .....	6
3.3	Chloroethane Adsorption Equilibrium Data .....	9
3.4	Water Adsorption Equilibria .....	9
3.5	Ammonia Micro-Breakthrough .....	11
3.6	Cyanogen Chloride Micro-Breakthrough .....	13
3.7	Sulfur Dioxide Micro-Breakthrough .....	14
4.	CONCLUSIONS .....	16
5.	RECOMMENDATIONS .....	17
	LITERATURE CITED .....	19

## FIGURES

1.	Titania Delamination .....	2
2.	Titania Multiwalled Nanotubes.....	2
3.	Adsorption Equilibrium System Schematic.....	4
4.	Water Isotherm System.....	5
5.	Rapid Nanoporous Adsorbent Screening System.....	5
6.	Nitrogen Isotherm Plot.....	7
7.	Nitrogen Isotherm Log Plot .....	7
8.	Chloroethane Adsorption Equilibria at 25 °C – Volume Basis.....	10
9.	Water Adsorption Equilibria at 25 °C .....	10
10.	Ammonia Breakthrough Curves .....	12
11.	CK Breakthrough Curves.....	13
12.	SO <sub>2</sub> Breakthrough Curves.....	15

## TABLES

1.	Pore Characteristics of Titania Nanotubes.....	3
2.	Packing Density of Samples .....	6
3.	Fit Parameters for Calculated BET .....	8
4.	Calculated BET Surface Area and Porosity of Sorbents .....	8
5.	Volume of Nitrogen Adsorbed on Selected Materials – Mass Basis.....	8
6.	Volume of Nitrogen Adsorbed on Selected Materials – Volume Basis .....	9
7.	Moisture Loading of Sorbents at 25 °C.....	11
8.	Ammonia Dynamic Capacity of Sorbents .....	13
9.	CK Dynamic Capacity of Sorbents.....	14
10.	SO <sub>2</sub> Dynamic Capacity of Sorbents.....	16



# EVALUATION OF TITANIA NANOTUBES FOR THE REMOVAL OF TOXIC INDUSTRIAL CHEMICALS

## 1. INTRODUCTION

In February 2008, Professor Yue Wu's group at the University of North Carolina provided titania nanotubes to the U.S. Army Edgewood Chemical Biological Center (ECBC) for evaluation. Titania nanotubes have shown promise for incorporation into air purification technologies due to their extensive decontamination capabilities (Kleinhammes et al., 2005, Wagner et al., 2007, and Wagner et al., 2008). The objective of this evaluation was to assess the physical properties as well as the adsorptive and reactive capabilities of the titania nanotubes.

The evaluation of the titania nanotubes summarized in this report is part of a larger, Defense Threat Reduction Agency (DTRA)-funded effort to develop novel, nanoscale porous materials for use as sorbents in air purification applications. The objective of this effort is to evaluate the performance characteristics of novel sorbents against a variety of toxic industrial chemicals (TICs) and chemical warfare agents (CWAs) with an emphasis on highly reactive materials that possess broad spectrum filtration capabilities. The goal of this effort is either to develop materials capable of providing better/broader protection than our current filtration material, ASZM-TEDA, or to complement its filtration properties, possibly leading to composite filters with tailorable performance. If successful, this approach should enable development of materials and filter designs to purify air via first principles.

## 2. EXPERIMENTAL PROCEDURES

### 2.1 Samples Evaluated

The titania nanotubes studied in this effort have the empirical formula  $\text{H}_2\text{Ti}_3\text{O}_7$  (or  $3\text{TiO}_2 \cdot \text{H}_2\text{O}$ ) (Wu, 2008). The possible benefit of nanotubes over typical nanocrystals is the extra availability of surface area due to irregular stacking (Kleinhammes et al., 2005). The nanotubes were synthesized using a novel process that delaminates anatase along the [001] direction. Anatase, one of three mineral forms of titania (the others being rutile and brookite), has shown extensive reactivity in catalyst applications (Gong and Selloni, 2005, Mogilevsky et al., 2008). A schematic of the topology of anatase and the delamination process are shown in Figure 1.

The delaminated anatase sheets are then formed into open-ended multiwalled nanotubes (MWNT), which can be thought of as concentric circles rolled up into an open-ended tubular structure (Ma et al., 2004 and Ma et al., 2005). These MWNTs provide a large pore opening in the middle of the concentric circles, as well as smaller pore openings between the concentric sheets (Kleinhammes et al., 2005). Figure 2 illustrates the (a) concentric circles of multi-walled nanotubes, and (b) SEM images of titania nanotubes from Mogilevsky et al.



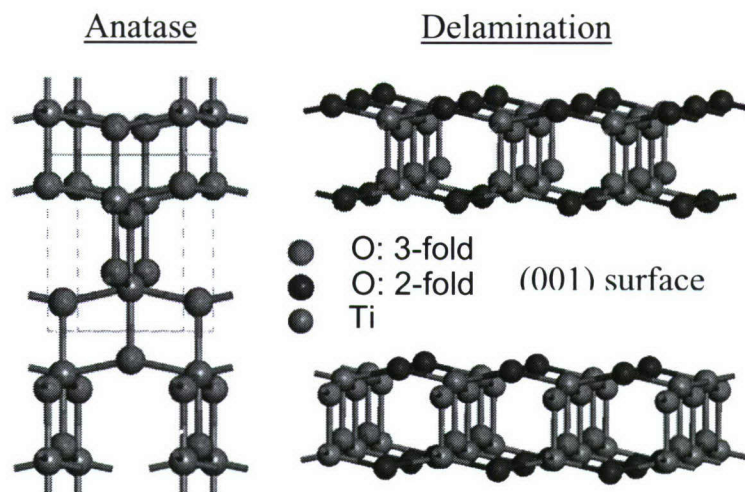


Figure 1. Titania Delamination

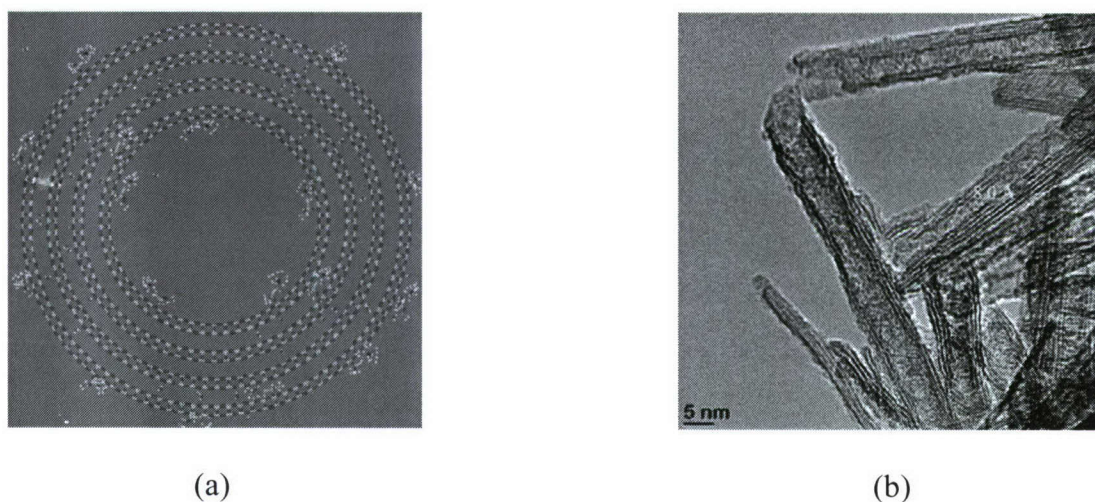


Figure 2. Titania Multiwalled Nanotubes

The pore characteristics of the titania nanotubes in Table 1 have been gathered from previous works on these materials (Kleinhammes et al., 2005 and Mogilevsky et al., 2008).

As summarized in Table 1, the nanotubes consist of both micropores and large mesopores, possibly providing adsorption sites for chemicals of interest.

Table 1. Pore Characteristics of Titania Nanotubes

Characteristic	Value
Inside diameter	4 – 5 nm
Outside diameter	10 – 12 nm
Space between sheets	7 – 8 Å

## 2.2 Testing Protocol

The titania nanotubes, as well as baseline ASZM-TEDA, were evaluated by collecting the following data:

- nitrogen isotherm
- packing density
- temperature and moisture stability
- nitrogen, chloroethane, and water adsorption equilibria
- micro-breakthrough testing

The packing density of the sample was determined to summarize data on a mass and volume basis. Samples were placed in a 10-mm OD glass tube. The resulting weight and volume were used to calculate the packing density.

Nitrogen isotherm data were collected with a Quantachrome Autosorb Automated Gas Sorption System. Approximately 20 mg of each sample was used for the analysis. Samples were outgassed at a temperature of 150 °C for at least 8 hr prior to data measurement. Nitrogen isotherm data were used to estimate the surface area, pore volume, and average pore size.

Chloroethane (CE) adsorption equilibrium (AE) data were collected at 25 °C for the titania nanotubes, and baseline samples on the system are illustrated in Figure 3. The equilibrium system uses a Fourier Transform Infrared (FTIR) spectrometer to determine the CE vapor phase concentration, and, by inference, the CE capacity at different relative pressures. Data are collected based on the vapor concentration difference pre- and post-chemical challenge to a pre-weighed adsorbent and measured volume (i.e., volumetric). Calibrated sample loops provide chemical to the volumetric system in precise quantities. The FTIR spectrometer measures the vapor concentration by partial least squares fit of single and multicomponent chemical vapor concentrations.

Water isotherms were collected on titania nanotubes and ASZM-TEDA at 25 °C. Water was delivered from a saturator cell to a temperature-controlled microbalance containing the sorbent to be evaluated. The concentration of moisture in the air, or relative humidity, was systematically increased (or decreased) by changing the temperature of the saturator cell. By measuring the change in weight, the amount of water adsorbed on the material was calculated. A system schematic is illustrated in Figure 4.



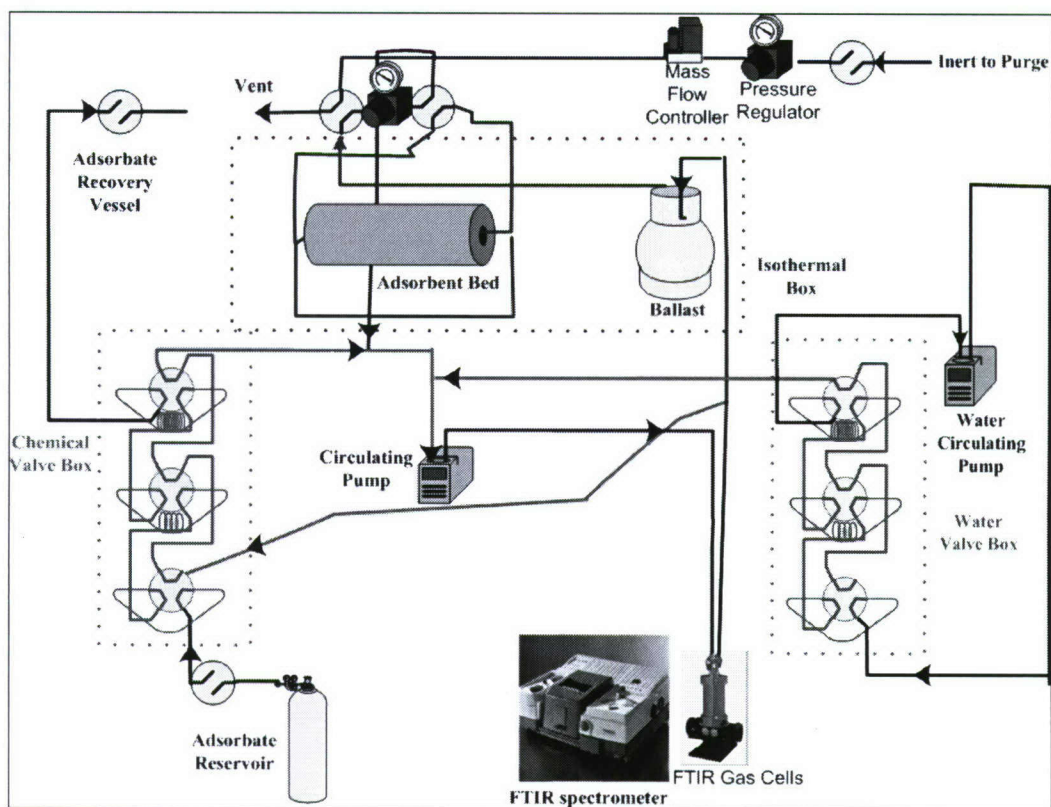


Figure 3. Adsorption Equilibrium System Schematic

Samples were evaluated for ammonia, cyanogen chloride (CK), and sulfur dioxide capacity using micro-breakthrough systems. A specific amount of chemical was injected into a ballast that was subsequently pressurized. This chemical mixture was then mixed with an air stream containing the required moisture content (from a temperature-controlled saturator cell) to achieve a predetermined concentration. The completely mixed vapor then passed through a sorbent bed submerged in a temperature-controlled water bath. Approximately 20 mg of each sample were tested under dry and humid conditions. The effluent stream then passed through a continuously operating gas chromatograph. A system schematic is shown in Figure 5.

Approximately 50 mm<sup>3</sup> of sorbent were evaluated using an ammonia challenge at a feed concentration of 800 mg/m<sup>3</sup> in air, a bed depth of 4 mm, a flow rate of 20 mL/min (referenced to 25 °C) through a 4 mm tube, and a relative humidity (RH) of approximately 0% (approximately -40 °C dew point). The residence time (bed volume divided by the flow rate) was approximately 0.15 sec. In all cases, sorbents were pre-equilibrated for 1 hr at the same relative humidity as the test. The effluent concentrations were monitored using a photoionization detector (PID).

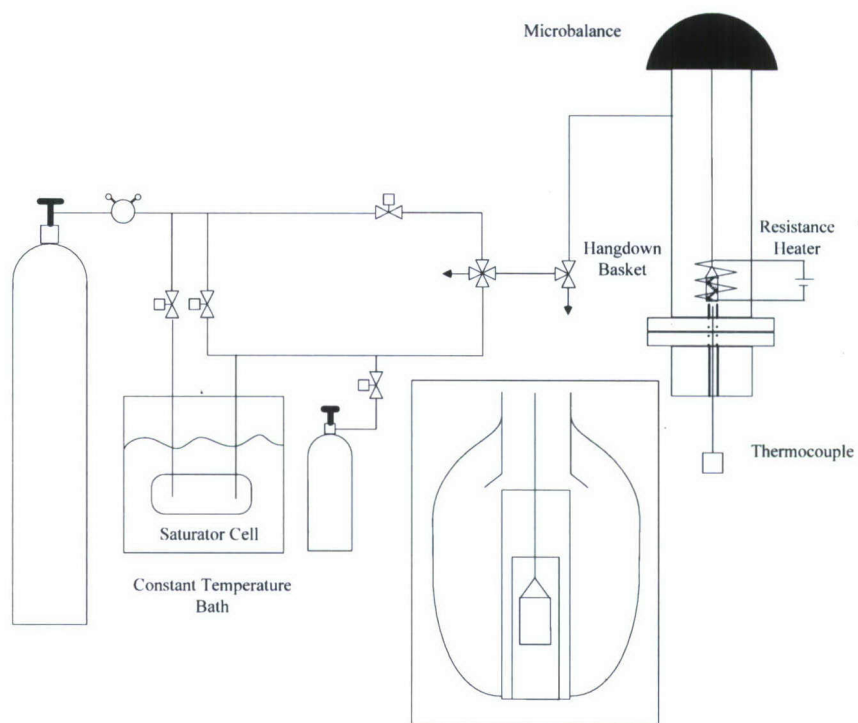


Figure 4. Water Isotherm System

### Rapid Nanoporous Adsorbent Screening System (RNASS)

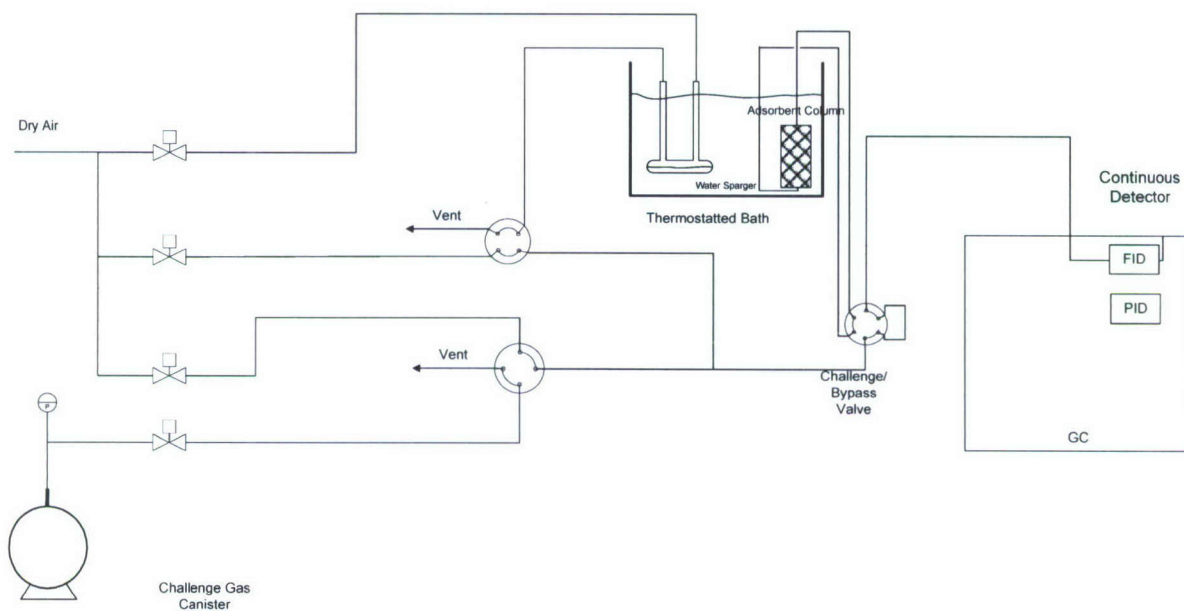


Figure 5. Rapid Nanoporous Adsorbent Screening System

Approximately 50 mm<sup>3</sup> of sorbent were evaluated using a cyanogen chloride (ClCN or CK) challenge at a feed concentration of 4,000 mg/m<sup>3</sup> in air, a flow rate of 20 mL/min (airflow velocity of approximately 3 cm/sec) referenced to 25 °C, a temperature of 20 °C, and at approximately 0% and 80% RH. In all cases, sorbents were pre-equilibrated for approximately 1 hr at the same relative humidity as the test. The effluent concentrations were monitored with an HP5890 Series II Gas Chromatograph equipped with a flame ionization detector (GC/FID).

Approximately 50 mm<sup>3</sup> of sorbent were evaluated with sulfur dioxide at a feed concentration of 1,000 mg/m<sup>3</sup>, a flow rate of 20 mL/min referenced to 25 °C, a temperature of 20 °C, and at approximately 0% and 80% RH. In all cases, sorbents were pre-equilibrated for 1 hr at the same relative humidity as the test. The concentration eluting through the sorbent was monitored with an HP5890 Series II GC/FPD.

### 3. RESULTS AND DISCUSSION

#### 3.1 Packing Density

The packing density of each sample was calculated to summarize data on a mass and volume basis. Although data are typically reported on a mass basis, filters are designed on a volume basis. The packing density was determined by placing each material in a 10-mm OD glass tube and then dividing the dry weight by the volume of the material. Packing density measurements are summarized in Table 2.

Table 2. Packing Density of Samples

Sample	Approximate Mesh	Packing Density
Titania Nanotubes	Powder, < 70	0.57 g/cc
ASZM-TEDA	12x30	0.61 g/cc

\*An actual sieve analysis was not conducted - particle mesh was estimated.

The titania nanotubes have a similar packing density to ASZM-TEDA. All filters are filled by volume and not mass. Therefore, all properties are reported on a mass and a volume basis.

#### 3.2 Nitrogen Isotherm

Nitrogen isotherm data were collected with a Quantachrome Autosorb Automated Gas Sorption System. Approximately 20 mg of each sample was used for the analysis. Samples were outgassed at a temperature of 150 °C for at least 8 hr. Nitrogen isotherm data were collected over six orders of magnitude of relative pressure and were then used to estimate the surface area, pore volume, and average pore size of the samples. Data are illustrated in Figures 6 and 7.



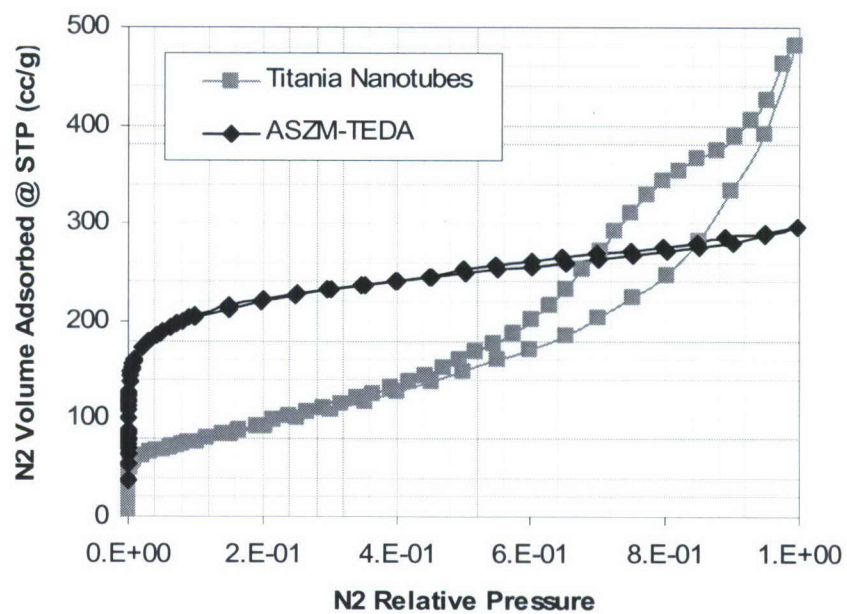


Figure 6. Nitrogen Isotherm Plot

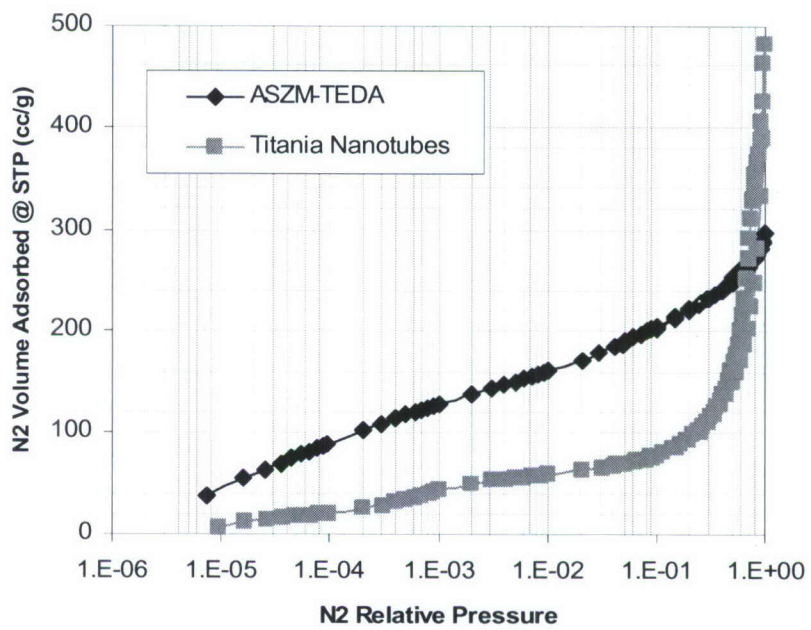


Figure 7. Nitrogen Isotherm Log Plot

The titania nanotubes exhibit very different adsorption behavior than ASZM-TEDA; whereas the ASZM-TEDA N<sub>2</sub> isotherm conforms to Type I, the nanotubes behave more like a Type II. This behavior makes sense with respect to the type of pores present in the titania nanotubes. At very low relative pressures, there may be initial pore filling of the small pores between the multiwall layers as well as monolayer coverage in the main pore. At higher relative pressures, a dramatic increase in nitrogen sorption occurs on the nanotubes due to multi-layer adsorption. The large amount of sorbed nitrogen gives way to bulk fluid-like properties, which is the likely cause of the hysteresis seen in Figure 6. Data presented in Figure 7 show that over most of the relative pressure range, ASZM-TEDA provides more sorption capacity than the nanotubes; however, the nanotubes have a larger pore volume. From the nitrogen isotherm plots, values were calculated for  $1/[W((P_0/P)-1)]$  and plotted against relative pressure to calculate BET surface area. These values are summarized in Table 3.

Table 3. Fit Parameters for Calculated BET

Sample	Slope	Y-Intercept	R <sup>2</sup>	C
Titania Nanotubes	10.81	0.07864	0.999902	138.4
ASZM-TEDA	4.224	0.01043	0.999971	406.1

Nitrogen isotherm data were used to calculate the BET surface and total pore volume. The packing density was used to calculate the values on a mass and volume basis. Table 4 summarizes the calculated values, and Tables 5 and 6 summarize the amount of nitrogen adsorbed at various relative pressures.

Table 4. Calculated BET Surface Area and Porosity of Sorbents

Sample	BET Surface Area		Pore Volume	
	m <sup>2</sup> /g-adsorbent	m <sup>2</sup> /cm <sup>3</sup> -adsorbent	cm <sup>3</sup> -N <sub>2</sub> /g-adsorbent	cm <sup>3</sup> -N <sub>2</sub> /cm <sup>3</sup> -adsorbent
Titania Nanotubes	320	180	0.75	0.43
ASZM-TEDA	820	500	0.46	0.28

Table 5. Volume of Nitrogen Adsorbed on Selected Materials – Mass Basis

Samples	Volume N <sub>2</sub> Adsorbed (cm <sup>3</sup> -STP/g-sorbent)			
	P/P <sub>0</sub> = 0.001	P/P <sub>0</sub> = 0.01	P/P <sub>0</sub> = 0.1	P/P <sub>0</sub> = 0.3
Titania Nanotubes	42.7	58.5	77.1	110
ASZM-TEDA	128	161	205	233

Table 6. Volume of Nitrogen Adsorbed on Selected Materials – Volume Basis

Samples	Volume N <sub>2</sub> Adsorbed (cm <sup>3</sup> -STP/cm <sup>3</sup> -sorbent)			
	P/P <sub>0</sub> = 0.001	P/P <sub>0</sub> = 0.01	P/P <sub>0</sub> = 0.1	P/P <sub>0</sub> = 0.3
Titania Nanotubes	24.3	33.3	43.9	62.7
ASZM-TEDA	78.1	97.9	125	142

### 3.3 Chloroethane Adsorption Equilibrium Data

Chloroethane adsorption equilibrium (AE) data were collected to assess the physical adsorption capacity of sorbent samples for light chemicals. Chloroethane was chosen as one of the chemicals of interest due to its similar physical properties with CK, a chemical that is historically filtration-limiting on military air purification sorbents. Chloroethane and CK generally have similar physical adsorption behavior but dissimilar reactive behavior. Thus, the potential to differentiate physical and reactive behavior exists. Adsorption equilibrium data for titania nanotubes and ASZM-TEDA baseline samples are shown in Figures 8 and 9.

Although the chloroethane adsorption data onto the titania nanotubes are a little jumpy, the trends are evident. Similar to the nitrogen isotherms, at low relative pressures, ASZM-TEDA exhibits favorable chloroethane adsorption while the nanotubes exhibit relatively unfavorable adsorption. As the chloroethane partial pressure increases, more chloroethane is adsorbed in the nanotubes as the amount adsorbed on ASZM-TEDA levels off.

### 3.4 Water Adsorption Equilibria

Water AE were collected on the samples using a Cahn microbalance to assess the moisture uptake at a full range of relative humidity (RH) conditions. These data are used to determine if titania nanotubes preferentially adsorb water as opposed to toxic chemicals. Additionally, hysteresis data can be used to determine pore interconnectivity. The AE data for the titania nanotubes and baseline samples are shown in Figure 9.

The data presented in Figure 9 show that at lower relative humidity conditions, the titania nanotubes pick up more moisture than ASZM-TEDA. This phenomenon is likely due to hydroxyl groups on the surface of the multi-layered nanotubes attracting water molecules through hydrogen bonding. At higher relative humidity conditions (60-90%), ASZM-TEDA picks up more moisture than the titania nanotubes; however, the capacity at saturation seems to be very similar.



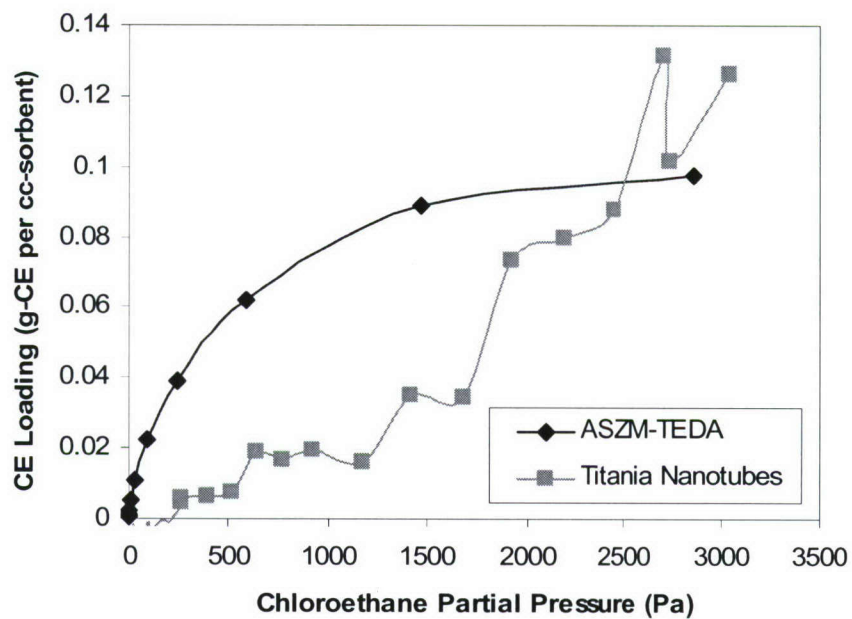


Figure 8. Chloroethane Adsorption Equilibria at 25 °C – Volume Basis

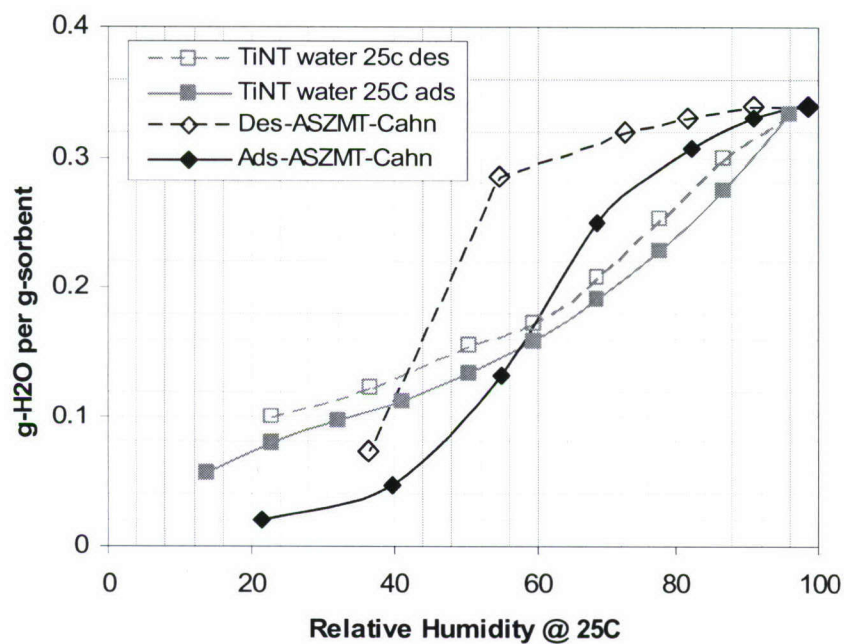


Figure 9. Water Adsorption Equilibria at 25 °C

Unlike ASZM-TEDA, although a hysteresis loop is present on the nanotubes, there is not a large difference between the adsorption loading and the desorption loading. Depending on the actual cause of hysteresis, this behavior is strange. One school of thought is that hysteresis is a measure of pore connectivity – when desorbing, the properties of water are more consistent with a bulk phase (as opposed to a sorbed phase), causing a discrepancy between the loadings. However, the data collected here do not show this large discrepancy, even though there is no question of the pore connectivity of the nanotubes, as a nanotube is essentially one large pore. Another possible cause for the hysteresis is that there was not enough time for the water loading to reach equilibrium. Table 7 summarizes the moisture loadings at three relative humidity conditions.

Table 7. Moisture Loading of Sorbents at 25 °C

Sample	Water Loading (g-water/g-sorbent)		
	15% RH	50% RH	80% RH
Titania Nanotubes	0.060	0.132	0.239
ASZM-TEDA	0.015	0.088	0.279

### 3.5 Ammonia Micro-Breakthrough

Ammonia micro-breakthrough testing was conducted on samples under dry and humid conditions to assess ammonia reactive capacity and, more generally, the removal capacity of the titania nanotubes for basic/base-forming gases. ASZM-TEDA was run as a baseline sample and has a limited ammonia removal capacity. Approximately 50 mm<sup>3</sup> of sorbent were tested at a feed concentration of 800 mg/m<sup>3</sup> in air, a flow rate of 20 mL/min (referenced to 25 °C) through a 4-mm tube, and relative humidity conditions of approximately 0% and 80%. In all cases, sorbents were pre-equilibrated for 1 hr at the same relative humidity as the test. The feed and effluent concentrations were monitored with a PID. Ammonia breakthrough curves under dry relative humidity conditions are illustrated in Figure 10.

Under dry and humid relative humidity conditions, the titania nanotubes exhibit better ammonia performance than ASZM-TEDA. The poor performance of ASZM-TEDA is expected, as there are no removal mechanisms for ammonia other than possible weak interactions with copper carbonate and very weak, reversible physical adsorption. The removal capability of the titania nanotubes was somewhat surprising; however, recent studies by Toledo-Antonio and coworkers (2007), as well as Mogilevsky and coworkers (2008), have shown terminal hydroxyls on the titania nanotube surface due to interactions with water. It is possible that the presence of hydroxyl groups promoted hydrogen bonding with ammonia, leading to a reversible removal mechanism. This behavior is substantiated by the long desorption curve after feed termination, indicating weakly bonded ammonia molecules off-gassing from the nanotubes.



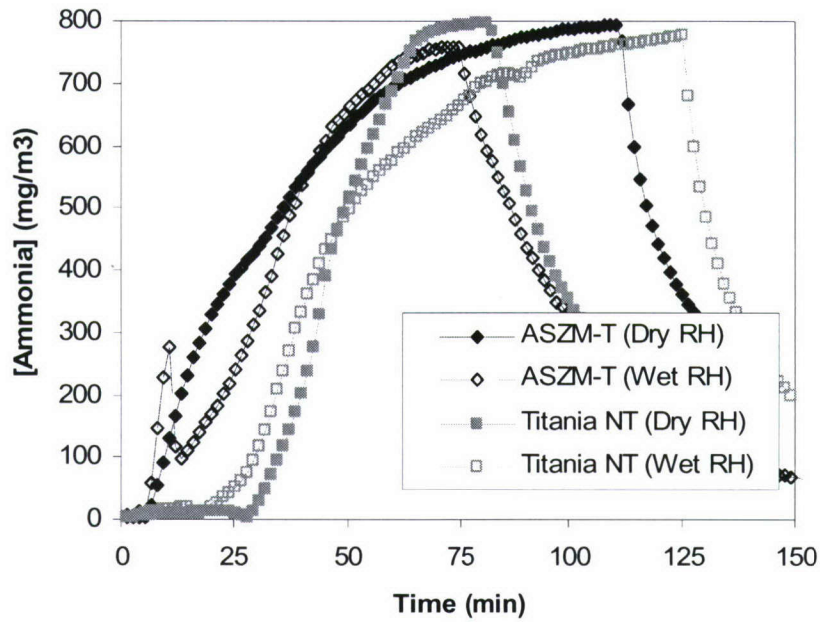


Figure 10. Ammonia Breakthrough Curves  
[Ammonia]  $\sim 800 \text{ mg/m}^3$

Ammonia breakthrough data were used to calculate the dynamic capacity to the stoichiometric center of the breakthrough curve using eqs. 1 and 2. The results are summarized in Table 8.

$$Ct = t_B * [Feed] \quad (1)$$

where

$$Ct = \text{mg-min/m}^3$$

$$t_B = \text{Breakthrough time [=] min}$$

$$[Feed] = \text{Feed concentration [=] mg/m}^3$$

$$W_D = \frac{Ct * FR}{Mass} \quad (2)$$

where

$$W_D = \text{Dynamic capacity [=] g ammonia per g sorbent}$$

$$FR = \text{Flow rate [=] m}^3/\text{min}$$

$$Mass = \text{Mass of sorbent [=] mg}$$

Table 8. Ammonia Dynamic Capacity of Sorbents

Sample	Sorbent Mass *	Breakthrough Time to S.C.	$W_D$ to 500 mg/m <sup>3</sup>	
			Mass Basis	Volume Basis *
Titania Nanotubes (Dry)	21.8 mg	46 min	0.033 g/g	0.019 g/cc
Titania Nanotubes (Wet)	18.3 mg	44 min	0.038 g/g	0.022 g/cc
ASZM-TEDA (Dry)	16.9 mg	27 min	0.025 g/g	0.015 g/cc
ASZM-TEDA (Wet)	17.3 mg	33 min	0.031 g/g	0.019 g/cc

\*Dry basis – does not include mass of loaded water

As Table 8 indicates, the titania nanotubes studied in this effort have a slightly better ammonia removal capacity than ASZM-TEDA on a mass and volume basis.

### 3.6 Cyanogen Chloride (CK) Micro-Breakthrough

Cyanogen chloride micro-breakthrough testing was conducted on samples under dry and humid conditions to assess CK reactive capacity. In addition to information on CK removal capabilities, breakthrough curves should indicate the ability of titania nanotubes to remove acid gases. The ASZM-TEDA was run as a baseline sample and has a relatively high CK removal capacity. Approximately 50 mm<sup>3</sup> of sorbent were tested at a feed concentration of 4,000 mg/m<sup>3</sup>, a flow rate of 20 mL/min (airflow velocity of approximately 3 cm/sec) referenced to 25 °C, a temperature of 20 °C, and relative humidities of approximately 0% and 80%. In all cases, sorbents were pre-equilibrated for approximately 1 hr at the same RH as the test. The feed and effluent concentrations were monitored with an HP5890 Series II GC/FID. Cyanogen chloride breakthrough curves for titania nanotubes and baseline ASZM-TEDA samples under low relative humidity conditions are illustrated in Figure 11.

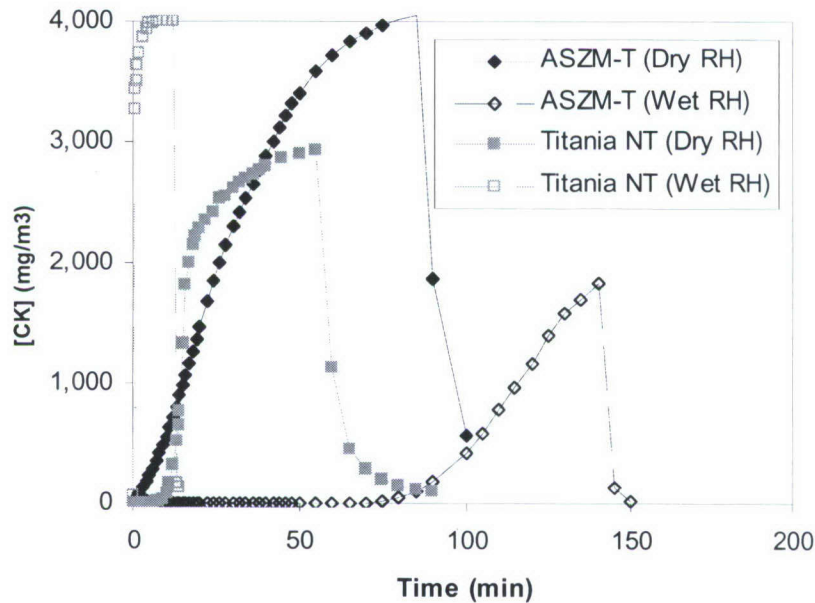


Figure 11. CK Breakthrough Curves  
[CK Challenge] = 4,000 mg/m<sup>3</sup>

The ASZM-TEDA and titania nanotubes exhibit some uptake of CK under low relative humidity conditions. The shallow ASZM-TEDA breakthrough curve can be attributed to the relatively large particle size (~12-30 US mesh size or 1.7-0.6 mm, respectively) as compared to the nanotubes tested. Under the dry relative humidity conditions, there may be some chemical reaction on ASZM-TEDA. However, the primary mechanism for removal is likely physical adsorption, as the effluent concentration does not return to zero immediately following termination of CK challenge. However, the nanotubes do seem to exhibit a permanent CK removal mechanism as the effluent concentration drops close to the baseline soon after feed termination.

Under humid relative humidity conditions, ASZM-TEDA is much more effective at removing CK than the titania nanotubes, which exhibit essentially no removal properties. Whereas, some CK was likely removed by the nanotubes under dry relative humidity conditions through a surface reaction/interaction with hydroxyl groups, these groups are covered with adsorbed moisture at high relative humidity conditions, rendering them useless for reaction with CK.

Cyanogen chloride breakthrough data were used to calculate the dynamic capacity of the sorbents to the stoichiometric center using the same methodology as was used for ammonia. Results are summarized in Table 9.

Table 9. CK Dynamic Capacity of Sorbents

Sample	Sorbent Mass*	Breakthrough Time to S.C.	$W_D$ to 2,000 mg/m <sup>3</sup>	
			<i>Mass Basis</i>	<i>Volume Basis</i> *
Titania Nanotubes (Dry)	20.2 mg	17 min	0.067 g/g	0.038 g/cc
Titania Nanotubes (Wet)	31.4 mg	0 min	0.000 g/g	0.000 g/cc
ASZM-TEDA (Dry)	15.1 mg	26 min	0.138 g/g	0.084 g/cc
ASZM-TEDA (Wet)	67.3 mg	143 min	0.170 g/g	0.104 g/cc

\*Dry basis – does not include mass of loaded water

As indicated in Table 9, although ASZM-TEDA has a better CK removal capacity, the nanotubes also have removal capabilities under dry relative humidity conditions.

### 3.7 Sulfur Dioxide Micro-Breakthrough

Sulfur dioxide micro-breakthrough testing was conducted on titania nanotubes under dry and humid conditions to assess sulfur dioxide reactive capacity, and, more generally, the removal capacity of the nanotubes for weak acid gases. The assumption is that if the nanotubes show removal mechanisms for weakly acidic gases, then strong acids should also be removed. The ASZM-TEDA was tested as a baseline sample and has a relatively high sulfur dioxide removal capacity. Approximately 50 mm<sup>3</sup> of sorbent were tested at a feed concentration of 1,000, a flow rate of 20 mL/min (airflow velocity of approximately 3 cm/sec) referenced to



760 Torr and 25 °C, a temperature of 20 °C, and relative humidities of approximately 0% and 80%. In all cases, sorbents were pre-equilibrated for 1 hr at the same relative humidity as the test. The concentration eluting through the sorbent was monitored with an FPD. Sulfur dioxide breakthrough curves for titania nanotubes and baseline samples are illustrated in Figure 12.

Under both relative humidity conditions, both materials exhibit some SO<sub>2</sub> removal capabilities. Although the breakthrough curves look similar in Figure 12, approximately three times as much mass of the titania nanotubes was used as compared to ASZM-TEDA, and therefore, the SO<sub>2</sub> capacity of ASZM-TEDA is much higher than that of the nanotubes. Under dry conditions, SO<sub>2</sub> is likely physically adsorbed on the nanotubes, as demonstrated by the relatively slow elution after feed termination. Likewise, there is also desorption seen under humid conditions, although after several minutes of desorption the SO<sub>2</sub> concentration drops to the baseline. This may be indicative of some formation of sulfuric acid, which does not elute due to its high boiling point and remains physically adsorbed on the nanotube surface.

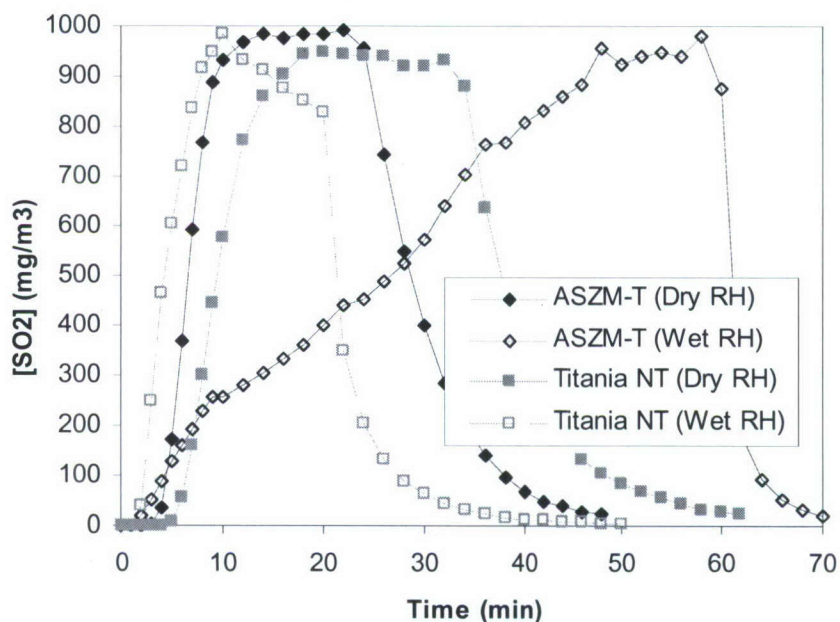


Figure 12. SO<sub>2</sub> Breakthrough Curves  
[Challenge] = 1,000 mg/m<sup>3</sup>

Sulfur dioxide breakthrough data were used to calculate the dynamic capacity using the same methodology as was used for ammonia. Results are summarized in Table 10.

Table 10. SO<sub>2</sub> Dynamic Capacity of Sorbents

Sample	Sorbent Mass*	Breakthrough Time to S.C.	W <sub>D</sub> to Stoichiometric Center*	
			<i>Mass Basis</i>	<i>Volume Basis</i> *
Titania Nanotubes (Dry)	17.7 mg	9.4 min	0.011 g/g	0.006 g/cc
Titania Nanotubes (Wet)	10.5 mg	4.2 min	0.008 g/g	0.005 g/cc
ASZM-TEDA (Dry)	5.2 mg	6.6 min	0.025 g/g	0.016 g/cc
ASZM-TEDA (Wet)	5.0 mg	26.5 min	0.105 g/g	0.065 g/cc

\*Dry basis – does not include mass of loaded water

#### 4. CONCLUSIONS

Adsorption equilibria, stability, and breakthrough testing have been performed to evaluate filtration performance of titania nanotubes and determine their usefulness in air purification applications. Several conclusions have been drawn from the data collected during this study and are summarized as follows:

- Nitrogen isotherm data were collected on titania nanotubes. Data conform to a Type II isotherm, with initial pore filling at low relative pressures between the multi-walled nanotube layers and high volumes of nitrogen adsorbed at high relative pressures due to multi-layer adsorption. The calculated BET surface area is approximately 320 m<sup>2</sup>/g, approximately two to three times less than ASZM-TEDA. However, the pore volume of the nanotubes is calculated to be approximately 0.75 c<sup>3</sup>/g, almost two times greater than ASZM-TEDA.
- The chloroethane equilibrium adsorption data were measured up to a partial pressure of approximately 3000 Pa. Data indicate that at low partial pressures, ASZM-TEDA adsorbs significantly more chloroethane than the titania nanotubes. At higher partial pressures, however, the nanotubes begin to adsorb greater quantities of chloroethane due to the larger available pore volume.
- Water adsorption data were measured up to a relative humidity (RH) of 95-97%. At lower relative humidity conditions, the titania nanotubes pickup more moisture than ASZM-TEDA, likely due to hydroxyl groups on the nanotube surface. At higher relative humidity conditions (60-90%), ASZM-TEDA picks up more moisture than the titania nanotubes; however, the capacity for both sorbents at saturation seems to be very similar.
- Ammonia breakthrough data were measured to determine nanotube capacity for basic gases. Under dry and humid relative humidity conditions, the titania nanotubes exhibit better ammonia performance than ASZM-TEDA. The presence of hydroxyl groups likely promoted hydrogen bonding with ammonia, leading to a reversible removal mechanism.



- Cyanogen chloride (CK) breakthrough data were measured to determine nanotube capacity for blood agents and difficult-to-remove acid gases. Although ASZM-TEDA provides better CK removal, the nanotubes exhibited some removal capabilities at low relative humidity conditions by physical adsorption. At high relative humidity conditions, however, the titania nanotubes had no CK capacity, with breakthrough occurring immediately.

- Sulfur dioxide breakthrough data were measured to determine nanotube capacity for acidic/acid-forming gases. Under low and high relative humidity conditions, nanotubes provide some SO<sub>2</sub> removal, albeit significantly less than ASZM-TEDA.

## 5. RECOMMENDATIONS

Based on results from evaluating the titania nanotubes studied in this effort, it is apparent that they do not provide substantial chemical removal capabilities as provided. Although the nanotubes did have a slightly better ammonia removal capacity than ASZM-TEDA, it is not significant enough to move forward as an engineered material. However, due to the large pore volume and surface chemistry of the nanotubes, there may be opportunities to functionalize the surface to provide removal mechanisms for either specific or a wide range of chemicals. It is recommended that steps be taken to functionalize the surface and resubmit samples for additional screening.

Blank

## LITERATURE CITED

Kleinhammes, A.; Wagner, G.; Kulkarni, H.; Jia, Y.; Zhang, Q.; Qin, L.; Wu, Y. Decontamination of 2-chloroethyl ethylsulfide using Titania nanotubes. *Chemical Physical Letters* **2005**, *411*, pp 81-85.

Wagner, G. W.; Wu, Y.; Kleinhammes, A. Nanotubular Titania for Decontamination of Chemical Warfare Agents. US Patent Applied for January 30, 2007.

Wagner, G. W.; Qiang, C.; Wu, Y. Reactions of VX, GD, and HD with Nanotubular Titania. Submitted to *J. Am. Chem. Soc.* 27 March 2008.

Wu, Yue. *Titania Nanotubes and Nanosheets: Synthesis, Properties, and Applications*. Presented at Colloquium, U.S. ArmyEdgewood Chemical Biological Center, Aberdeen Proving Ground, MD, January 2008.

Gong, X.; Selloni, A. Reactivity of Anatase TiO<sub>2</sub> Nanoparticles: The Role of the Minority (001) Surface. *J. Phys. Chem. B* **2005**, *109*, pp 19560-19562.

Mogilevsky, G.; Chen, Q.; Kulkarni, H.; Kleinhammes, A.; Mullins, W. M.; Wu, Y. Layered Nanostructures of Delaminated Anatase: Nanosheets and Nanotubes. *J. Phys. Chem. C* **2008**, *112*, pp 3239-3246.

Ma, R.; Bando, Y.; Sasaki, T. Directly Rolling Nanosheets into Nanotubes. *J. Phys. Chem. B* **2004**, *108*, pp 2115-2119.

Ma, R.; Fukuda, K.; Sasaki, T.; Osada, M.; Bando, Y. Structural Feature of Titania Nanotubes/Nanobelts Revealed by Raman, X-ray Absorption Fine Structure and Electron Diffraction Characterizations. *J. Phys. Chem. B* **2005**, *109*, pp 6210-6214.

Toledo-Antonio, J. A.; Capula, S.; Cortes-Jacome, M. A.; Angeles-Chaves, C.; Lopez-Salinas, E.; Ferrat, G.; Navarrete, J.; Escobar, J. Low-Temperature FTIR Study of CO Adsorption on Titania Nanotubes. *J. Phys. Chem. C* **2007**, *111*, pp 10799-10805.